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Article

Preparation of magnetic nanocomposites of solid acid catalysts and their applicability in esterification

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ABSTRACT

Solid acid catalysts are superior to traditional liquid acids because they are noncorrosive, environmentally benign, and recyclable. In addition, nano-magnetic solid acid catalysts are preferable as they exhibit large specific surface areas together with good acidity and are also readily separated from the post-reaction mixture. Three component nano-magnetic solid catalysts TiO_2-Al_2O_3-Fe_3O_4 and CeO_2-Al_2O_3-Fe_3O_4 and a four component catalyst ZrO_2-Al_2O_3-CeO_2-Fe_3O_4 were synthesized by a co-precipitation method and were subsequently characterized by inductively coupled plasma-atomic emission spectroscopy, Brunauer-Emmett-Teller surface area analysis, X-ray diffraction, transmission electron microscopy, and thermal gravimetric analysis. Their catalytic activities were also evaluated in the esterification reaction of acetic acid with *n*-butanol. The results demonstrated that these rare earth-based magnetic nanocomposites exhibited good catalytic activity.

1. Introduction

Acid catalysts have numerous applications in various industrial organic reactions, and homogenous acids such as H_2SO_4, HCl, and HF have been widely used in chemical engineering. However, these mineral acids have serious drawbacks in terms of difficulties in post-reaction separation and negative environmental impact, as well as their tendency to contribute to the corrosion of reactors. Over the last few decades, many different solid acid catalysts have been developed as alternatives, including metal oxides, zeolites, metal phosphates, and sulfated metal oxides [1–5], and these are widely used in alkylation [6], esterification [7,8], isomerization [9,10], nitration [11], and other reactions. In addition, it is well known that sulfated solid acids (SO_4^{2-}/MO_x) are potential candidates for the development of environmentally benign organic syntheses. Unfortunately, the activity of these materials decreases significantly during use because of sulfur reduction and the formation of surface coke [12–15], hindering their industrial applications. Therefore, there is still a need to develop environmentally benign catalysts with high activity.

Typically, these heterogeneous catalysts are separated by labor-intensive filtration or centrifugation processes. Hence, much research has been devoted to the development of easily separable heterogeneous catalysts. Magnetic nanoparticles (MNPs) have been extensively researched with regard to their applications in disciplines, including magnetic resonance imaging [16], magnetic storage media [17], biotechnology [18], and ferrofluids [19]. Among these magnetic materials, Fe_3O_4 nanoparticles have been used as a versatile support for a variety of heterogeneous catalysts in different types of organic transformations [20].

Based on the above factors and our own previous research results [15], we have designed and synthesized several series of "green" solid acids, TiO_2-Al_2O_3-Fe_3O_4 (TAF), CeO_2-Al_2O_3-Fe_3O_4 (CAF), and ZrO_2-Al_2O_3-CeO_2-Fe_3O_4 (ZACF), each of which

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has been applied to the esterification reaction between a carboxylic acid and an alcohol. We subsequently identified the best catalyst (i.e., that exhibiting the highest activity) by varying the molar ratio of different oxides in the catalyst. Furthermore, we propose a plausible mechanism for the esterification reaction based on characterization of the structures and morphologies of these materials.

2. Experimental

2.1. Preparation of catalysts

$ZrOCl_2·8H_2O$, $AlCl_3·6H_2O$, $Ce(SO_4)_2·4H_2O$, *n*-butanol, acetic acid, tetrabutyl titanate, and toluene were all obtained from commercial sources and used as-received without further purification.

Fe_3O_4 MNPs were generated by dissolving $FeCl_3·6H_2O$ (6.76 g) and $FeSO_4·7H_2O$ (3.80 g) in 100 mL of deionized water to produce a clear solution, following which the pH was adjusted to 10 with NH_4OH acting as a precipitant. After 2 h of vigorous stirring at 60 °C, the precipitate was separated magnetically and then washed with deionized water and ethanol. The resulting black, magnetic solid was dried under vacuum at room temperature (Fig. 1).

TAF-4/4 (4/4 means that the molar ratio of $TiO_2/Al_2O_3/Fe_3O_4$ is 4:4:1) was obtained by dissolving $AlCl_3·6H_2O$ (4 mmol) and tetrabutyl titanate (4 mmol) in 100 mL of ethanol to produce a clear solution, after which Fe_3O_4 MNPs (0.2314 g) were added with ultrasonic agitation for 30 min. NH_4OH was subsequently added as precipitant while adjusting the pH to 9.2. After 12 h of vigorous stirring at room temperature, the precipitate was filtered, washed with deionized water, and dried overnight at 80 °C in a vacuum oven. The remaining nano-magnetic catalysts were also synthesized using this same method.

2.2. Characterization of catalysts

Inductively coupled plasma-atomic emission spectroscopy (ICP-AES) data were collected using an IRIS ER/S emission spectrometer (American TAJ Co.). N_2 adsorption-desorption isotherms were recorded at −195.8 °C on a TriStar II 3020V instrument. The specific surface areas of the materials were calculated using the Brunauer-Emmett-Teller (BET) equation over a range of relative pressure ratios (p/p_0) from 0.06 to 0.3. Powder X-ray diffraction (XRD) patterns were obtained with an X'Pert PRO diffractometer (Holland PANalytical Co.) over the range of 2θ = 20°–90° at a scan rate of 8°/min using Cu K_α radiation (λ = 0.15406 nm). Transmission electron microscope

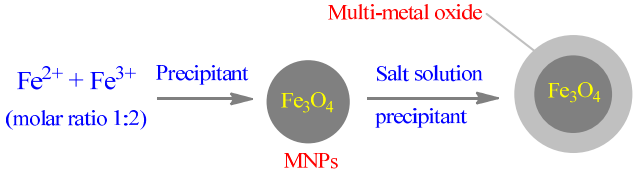
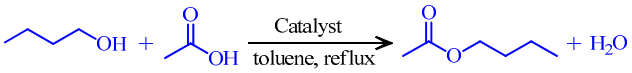


Fig. 1. Preparation of nano-magnetic catalysts.



Scheme 1. Esterification of acetic acid with *n*-butanol.

(TEM) and high resolution TEM (HRTEM) images were obtained using a field emission TEM (Tecnai-G2-F30). Fourier transform infrared (FT-IR) spectra were acquired on a Nicolet NEXUS 670 over the range of 400 to 4000 cm^{-1} with a resolution of 4 cm^{-1}. Thermal gravimetric (TG) analyses were performed under N_2 from room temperature to 600 °C at a heating rate of 10 °C/min using a Linseis STA PT 1600 thermoanalyzer.

2.3. Typical procedure for the esterification reaction of acetic acid with n-butanol

Acetic acid (0.075 mol), *n*-butanol (0.050 mol), catalyst (0.5 g), and 25 mL toluene were combined in a 50 mL flask along with a magnetic bar and water separator. The flask was then immersed in an oil bath and heated to reflux. During the reaction, produced water was separated by the water separator. After the reaction, the catalyst was detached from the flask with magnets for recycling, and the conversion (yield) was determined by GC with FID (Scheme 1)

3. Results and discussion

3.1. Characterization results

The ICP-AES and BET specific surface areas results are shown in Table 1. When preparing TAF, the pH of the solution was approximately 9.2. At this pH, the reaction mixture contained a significant quantity of $Al(OH)_4^-$ and $Ti(OH)_n^-$ ions because these species do not precipitate completely at that pH value. The ICP-AES results show some variations between the actual and theoretical molar ratios due to the loss of Al and Ti through the formation of their same ions, as well as the incomplete precipitation of other metal ions at this pH value [21–23].

The XRD patterns of these catalysts are depicted in Fig. 2. In Fig. 2(a), there are only a few weak peaks from Fe_3O_4, showing

Table 1
ICP-AES data and specific surface areas of the catalysts.

Catalyst	ZrO_2 (TiO_2)-Al_2O_3-CeO_2-Fe_3O_4 molar ratio		S_{BET} (m^2/g)
	Theoretical	Measured[a]	
TAF-4/4	4:4:0:1	0.98:0.70:0:1	358.72
TAF-8/8	8:8:0:1	1.69:1.28:0:1	256.50
TAF-12/12	12:12:0:1	2.26:1.79:0:1	54.84
TAF-16/16	16:16:0:1	3.26:2.67:0:1	365.99
CAF-8/8	0:8:8:1	0:2.48:0.99:1	196.24
CAF-12/12	0:12:12:1	0:3.84:0.73:1	192.72
CAF-16/16	0:16:16:1	0:5.05:1.42:1	104.56
ZAF-16/16	16:16:0:1	3.99:3.93:0:1	299.26
ZACF-16/16/2	16:16:2:1	4.33:5.36:0.69:1	268.30
ZACF-16/16/4	16:16:4:1	4.41:2.75:1.48:1	288.60
ZACF-16/16/6	16:16:6:1	5.01:4.29:2.05:1	224.05
ZACF-16/14/2	16:14:2:1	4.08:3.43:0.70:1	271.85

[a] Determined by ICP-AES analysis.